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High-strength martensitic stainless steel and method for making the same.

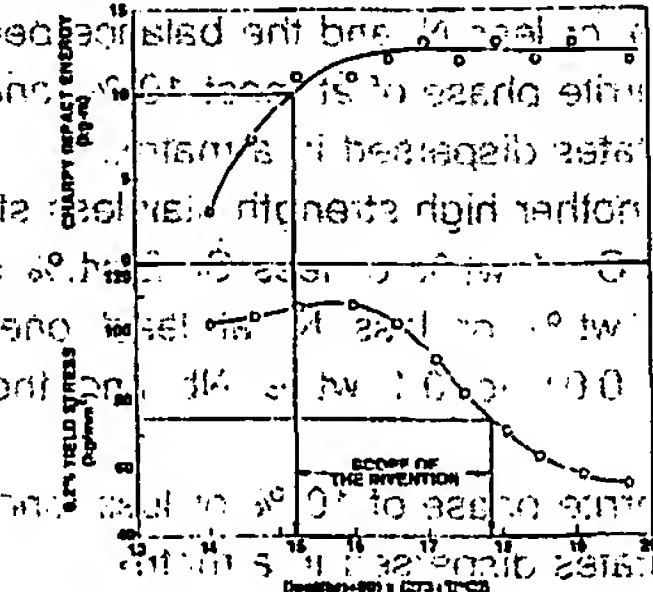
A high strength martensitic stainless steel contains:

0.06 wt.% or less C, 12 to 16 wt.% Cr, 1 wt.% or less Si, 2 wt.% or less Mn, 0.5 to 8 wt.% Ni, 0.1 to 2.5 wt.% Mo, 0.3 to 4 wt.% Cu, 0.05 wt.% or less N, and the balance being Fe and inevitable impurities;

said steel having an area ratio of δ -ferrite phase of at most 10 %; and
said steel having fine copper precipitates dispersed in a matrix.

And further a method for making the stainless steel comprises austenitizing, cooling and tempering.

FIGURE



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BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

5 The present invention relates to a high-strength martensitic stainless steel having excellent anti-stress corrosion cracking property and a method for making the same, and more particularly to a high-strength martensitic stainless steel showing excellent anti-stress corrosion cracking property in an environment containing CO₂ and H₂S in such a case of drilling and transporting crude oil and natural gas, and a method for making the same.

DESCRIPTION OF THE RELATED ARTS

10 Crude oil and natural gas recently extracted often contain large amounts of CO₂ and H₂S. To cope with this, martensitic stainless steels such as 13Cr stainless steel are adopted instead of conventional carbon steel.

15 Ordinary martensitic stainless steels, however, have superior corrosion resistance to CO₂ (hereinafter referred to simply as "corrosion resistance") but have insufficient stress-corrosion cracking resistance to H₂S (hereinafter referred to simply as "anti-stress corrosion cracking property"). Accordingly, a martensitic stainless steel having improved anti-stress corrosion cracking property while maintaining favorable strength, toughness, and corrosion resistance has long been wanted.

20 Materials which satisfy the requirements of strength, toughness, and corrosion resistance, and also of anti-stress corrosion cracking property are disclosed in Examined Japanese Patent Publication No. 61-3391, Unexamined Japanese Patent Publication No. 58-199850 and 61-207550. Those materials show a resistance to an environment containing only a slight quantity of H₂S, but they generate stress-corrosion cracking in an environment at over 0.01 atm. of H₂S partial pressure. So those materials can not be used in an environment containing a large amount of H₂S.

30 On the other hand, some of martensitic stainless steels which have an improved anti-stress corrosion cracking property in an environment exceeding 0.01 atm. of H₂S partial pressure are introduced. Examples of that type of martensitic stainless steel are disclosed in Unexamined Japanese Patent Publication Nos. 60-174859 and 62-54063. Those materials are, however, also unable to completely prevent stress corrosion cracking caused by H₂S.

From the viewpoint of strength, a trial for improving the strength on all the martensitic stainless steels described above resulted in a significant degradation of their toughness and anti-stress corrosion cracking property.

35 Accordingly, all those martensitic stainless steels have an unavoidable problem in that either toughness or anti-stress corrosion cracking property is sacrificed. As a result, those martensitic stainless steels can not be used as a deep OCTG (Oil Country Tubular Goods), for example, for which a high strength, anti-stress corrosion cracking property, anti-corrosion property, and toughness at the same time is requested.

40 SUMMARY OF THE INVENTION

It is an object of the present invention to provide a high-strength martensitic stainless steel which is applicable even in an environment containing a large amount of H₂S while maintaining corrosion resistance by improving the conventional martensitic stainless steel in terms of strength, anti-stress corrosion cracking property, and toughness at the same time, and provides a method for making thereof. To achieve the object, the present invention provides a high strength stainless steel consisting essentially of:

0.06 wt.% or less C, 12 to 16 wt.% Cr, 1 wt.% or less Si, 2 wt.% or less Mn, 0.5 to 8 wt.% Ni, 0.1 to 2.5 wt.% Mo, 0.3 to 4 wt.% Cu, 0.05 wt.% or less N, and the balance being Fe and inevitable impurities;

said steel having an area ratio of δ -ferrite phase of at most 10%; and

50 said steel having fine copper precipitates dispersed in a matrix.

And the present invention provides another high strength stainless steel consisting essentially of:

0.06 wt.% or less C, 12 to 16 wt.% Cr, 1 wt.% or less Si, 2 wt.% or less Mn, 0.5 to 8 wt.% Ni, 0.1 to 2.5 wt.% Mo, 0.3 to 4 wt.% Cu, 0.05 wt.% or less N, at least one element selected from the group consisting of 0.01 to 0.1 wt.% V and 0.01 to 0.1 wt.% Nb and the balance being Fe and inevitable impurities;

55 said steel having an area ratio of δ -ferrite phase of 10 % or less; and

said steel having fine copper precipitates dispersed in a matrix.

Moreover, the present invention provides a method for making a high strength stainless steel comprising the steps of:

- preparing a martensitic stainless steel consisting essentially of 0.06 wt.% or less C, 12 to 16 wt.% Cr, 1 wt.% or less Si, 2 wt.% or less Mn, 0.5 to 8 wt.% Ni, 0.1 to 2.5 wt.% Mo, 0.3 to 4 wt.% Cu, 0.05 wt.% or less N, and the balance being Fe and inevitable impurities;
- austenitizing said martensitic stainless steel at a temperature of A_{c3} transformation point to 980°C to produce an austenitized martensitic steel;
- cooling the austenitized martensitic stainless steel;
- tempering the cooled stainless steel to disperse fine Cu precipitate grains in a matrix at a tempering temperature ($T^\circ\text{C}$) of 500°C to lower one of either 630°C or A_{c1} transformation point and at a tempering time (t hour), said tempering temperature and said tempering time satisfying the following equation:

$$15200 \leq (20 + \log t)(273 + T) \leq 17800$$

And the present invention provides another method for making a high strength stainless steel comprising the steps of:

- preparing a martensitic stainless steel consisting essentially of 0.06 wt.% or less C, 12 to 16 wt.% Cr, 1 wt.% or less Si, 2 wt.% or less Mn, 0.5 to 8 wt.% Ni, 0.1 to 2.5 wt.% Mo, 0.3 to 4 wt.% Cu, 0.05 wt.% or less N, at least one element selected from the group consisting of 0.01 to 0.1 wt.% V and 0.01 to 0.1 wt.% Nb and the balance being Fe and inevitable impurities;
 - austenitizing said martensitic stainless steel at a temperature of A_{c3} transformation point to 980°C to produce an austenitized martensitic steel;
 - cooling the austenitized martensitic stainless steel;
 - tempering the cooled stainless steel to disperse fine Cu precipitate grains in a matrix at a tempering temperature ($T^\circ\text{C}$) of 500°C to lower one of either 630°C or A_{c1} transformation point and at a tempering time (t hour), said tempering temperature and said tempering time satisfying the following equation:
- $$15200 \leq (20 + \log t)(273 + T) \leq 17800$$

BRIEF DESCRIPTION OF THE DRAWING

FIGURE shows the relation of the 0.2% yield stress, the Charpy impact energy, and the temper parameter.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention provides a high-strength martensitic stainless steel which is applicable even in an environment containing a large amount of H_2S while maintaining corrosion resistance by improving the conventional martensitic stainless steel in terms of strength, anti-stress corrosion cracking property, and toughness at the same time, and provides a method for the manufacturing thereof. The target performance is specified as follows considering the requirements with regard to the drilling and transporting steel pipes for crude oil and natural oil which contain CO_2 and H_2S .

Strength: The 0.2% yield stress is 75 kg/mm² or more.

Toughness: Absorbed energy on a Charpy full size specimen at 0°C (called the Charpy impact energy) is 10 kg-m or more.

Anti-stress corrosion cracking property:

When a specimen is loaded at a 60% loading of the 0.2% yield stress in a mixture of 5% NaCl solution and 0.5% acetic acid aqueous solution saturated with H_2S gas of 1 atm, the specimen is durable for 720 hours or longer without failure.

Increasing the Cr is an effective means to improve the corrosion resistance of a martensitic stainless steel. However, the increase in the Cr content induces the generation of δ -ferrite phase which in turn, degrades the strength and toughness. Increasing the content of Ni which is an element of austenite phase generation acts as a countermeasure to that tendency by suppressing the formation of δ -ferrite phase. This method has, however, a limitation from the point of the cost of Ni. Also an increase in the C content is effective for suppressing the generation of δ -ferrite phase but it induces the generation of carbide during.

tempering which results in a degradation of the corrosion resistance. Consequently, the C content should be limited. Regarding the amount of δ -ferrite phase, when the area ratio thereof exceeds 10%, the presence of δ -ferrite phase has a negative effect on the strength and toughness. So the amount of δ -ferrite phase should be limited to 10% or less.

Generally, an increase in the strength of a steel degrades the toughness and anti-stress corrosion cracking property. However, the strength can be improved without degrading the toughness and anti-stress corrosion cracking property by introducing C in an adequate amount and by dispersing Cu as fine precipitate particles into the matrix of stainless steel through heat treatment. Since the precipitation of fine Cu particles requires the precise control of the tempering conditions, both the tempering temperature and the tempering time need to be controlled.

The present invention provides a novel martensitic stainless steel having high toughness and high strength and excellent anti-stress corrosion cracking property, which characteristics were not achieved in conventional martensitic stainless steels, while considering a restriction of the microstructure induced by the increased C content as discussed above.

The following are the reasons for the limitations of the present invention:

(1) C: 0.06% or less
Carbon binds with Cr in the tempering stage to precipitate as a carbide, which then degrades corrosion resistance, anti-stress corrosion cracking property, and toughness. Carbon content above 0.06% significantly enhances the degradation of those characteristics.

Therefore, the C content is specified as 0.06% or less.

(2) Cr: 12 to 16%

Chromium is a basic element to structure a martensitic stainless steel, and an important element to give corrosion resistance. However, a Cr content below 12% does not provide sufficient corrosion resistance, and that above 16% induces an increase of δ -ferrite phase which, in turn, leads to a degradation in the strength and toughness even when the other alloying elements are adjusted.

Accordingly, the content of Cr is specified to be within a range of from 12 to 16%.

(3) Si: 1.0% or less

Silicon, which functions as a de-oxidizer, is an essential element. But Si is a strong ferrite-generating element, and the presence of Si in an amount of more than 1.0% enhances the formation of δ -ferrite phase. Consequently, the Si content is specified as 1.0% or less.

(4) Mn: 2.0% or less
Manganese is effective as a de-oxidizer and a desulfurizing agent. Also, Manganese is effective as an austenite-generating element by suppressing the formation of δ -ferrite phase. However, excessive addition of Mn has a saturating effect, and therefore the Mn content is specified as 2.0% or less.

(5) Ni: 0.5 to 8.0%

Nickel is quite effective for improving corrosion resistance and for enhancing the formation of austenite phase. However, a Ni content below 0.5% does not have the effect. Since Ni is an expensive element, the upper limit of the Ni content is specified as 8.0%.

(6) Mo: 0.1 to 2.5%
Mo is a particularly effective element for improving corrosion resistance. However, a Mo content of less than 0.1% does not have the effect. A Mo content above 2.5% induces an excess amount of δ -ferrite phase, and so the upper limit of the Mo content is specified as 2.5%.

The present invention provides a high-strength martensitic stainless steel which contains a large amount of H₂ and which has excellent corrosion resistance and toughness. The present invention provides a high-strength martensitic stainless steel which contains a large amount of H₂ and which has excellent corrosion resistance and toughness. The present invention provides a high-strength martensitic stainless steel which contains a large amount of H₂ and which has excellent corrosion resistance and toughness.

(7) Cu: 0.3 to 4.0% (8) N: 0.05% or less (9) Additional components: V, Nb (V: 0.01 to 0.10%, Nb: 0.01 to 0.10%) (10) Area ratio of δ -ferrite phase: 10% or less (11) Fine precipitate of CuO (12) Austenitizing temperature: from A_{c3} point to 980°C (13) Tempering temperature: T_p ($^\circ\text{C}$) between 500°C and either the lower one of 630°C or A_{c1}

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(8) N: 0.05% or less: Nitrogen is an effective element for improving the corrosion resistance and also for generating austenite phase. However, a N content above 0.05% enhances the binding with Cr during tempering to precipitate as a nitride, which degrades the anti-stress corrosion cracking property and toughness. Consequently, the N content is specified as 0.05% or less. (9) Additional components: V, Nb (V: 0.01 to 0.10%, Nb: 0.01 to 0.10%): Vanadium and Niobium are powerful elements for forming carbides. They form a fine carbide precipitate to make crystal grains fine and improve the anti-stress corrosion cracking property. However, they are also the elements which form ferrite phase and increase the amount of δ -ferrite phase.

Accordingly, the content of each of them is specified to a range of from 0.01 to 0.10%. A content below 0.010% does not have the effect of improving the anti-stress corrosion cracking property, and that above 0.10% has a saturating effect and increases the amount of δ -ferrite phase which, in turn, has a negative effect on the toughness. Therefore, both V and Nb are limited to a range of from 0.01 to 0.10% each.

(10) Area ratio of δ -ferrite phase: 10% or less: The δ -ferrite phase is a phase which was not transformed to martensite during the quench/hardening of a martensitic steel and was left as ferrite phase. An increased amount of δ -ferrite phase significantly degrades the toughness. In that type of steel, if the area ratio of the δ -ferrite phase exceeds 10%, the degradation of the toughness is considerably enhanced. Accordingly, the upper limit of the area ratio of the δ -ferrite phase is specified as 10%.

(11) Fine precipitate of CuO: When precipitated in fine grains, Cu increases the strength of steel by the precipitation hardening effect without degrading the anti-stress corrosion cracking property which usually occurs along with the increase of the strength. The term "fine precipitate" refers to grains which are identifiable by observation under an electron microscope and which have an approximate size of 0.10 micron or less. When the Cu precipitate becomes coarse and exceeds 0.10 micron, however, the effect of improving the strength diminishes. Also when Cu does not precipitate and is left dissolved in the matrix, no improvement of the strength by precipitation hardening can be expected. Therefore, the Cu precipitate is specified as a fine precipitate. The dispersed amount is not specifically defined. Nevertheless, it is preferable that fine precipitation exists at a rate of 30 or more per 10^4 square micron of the matrix.

(12) Austenitizing temperature: from A_{c3} point to 980°C : A temperature below A_{c3} point results in an insufficient austenitizing and fails to obtain necessary strength. A temperature above 980°C induces the occurrence of coarse grains, significantly degrades toughness, and also decreases anti-stress corrosion cracking property. Therefore, the temperature range for austenitizing is specified to be from A_{c3} to 980°C . (13) Tempering temperature: T_p ($^\circ\text{C}$) between 500°C and either the lower one of 630°C or A_{c1}

Tempering is effective for softening the martensite structure to secure toughness and also for finely precipitating Cu into the matrix to increase the strength. However, if the tempering temperature is less than 500°C , the softening of the martensite structure is insufficient and the fine precipitation of Cu is insufficient,

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T : tempering temperature ($^{\circ}\text{C}$)

Now, the method for making the invention steel will be given. The steel of this invention is prepared in a converter or an electric furnace so as to have a composition range as specified in this invention. The steel is subjected to ingot casting process or continuous casting process to form an ingot. The ingot undergoes hot working into a seamless pipe or a steel sheet, which is then processed by heat treatment. The method of heat treatment is done as described above.

35 As for the composition of the steel of this invention, the additional component Al, W, Ti, Zr, Ta, Hf, Ca, or rare earth metal (REM) may be used. These additional elements can often contribute to the further improvement of the performance of the steel of this invention. The purpose and adequate content of these for individual elements are described below.

40 **Al:** Aluminium is added in order to effect oxygen removal, and the adequate content range is from 0.01 to 0.10%.

W: Tungsten is effective in CO₂ corrosion, while if it is added in an excess amount it degrades the toughness. Therefore, the maximum content is specified as 4%.

Ti, Zr, Ta, Hf: These elements are effective for improving the corrosion resistance, and an adequate content is max. 0.2%. The presence of these elements at more than 0.2% induces coarse grains which degrades

45 the anti-stress corrosion cracking property.

Ca, REM: These elements bind to S, a harmful impurity in steel, and significantly reduce damages of the steel; they also improve the anti-stress corrosion cracking property. Excessive amounts of these elements, however, have the reverse effect on the anti-stress corrosion cracking property, so the adequate content is specified to be 0.01% or less for Ca and to be 0.02% or less for REM.

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500° C. The softening of the material structure is sufficient, and the fine precipitation of Cu is insufficient precipitating Cu into the matrix to increase its strength. However, if the tempering temperature is less than 500° C. softening is effective in softening the material structure to secure the strength and size for further use and after the lower one in 685° C. or less.

EXAMPLE

The present invention is described in more detail in the following example. The inventors prepared test ingots of Example steels Nos. 1 to 13 and Comparative Example steels Nos. a to j. Those ingots were subjected to hot-rolling to form steel sheets having a thickness of 12 mm.

The steel sheets were then processed by heat treatment described below to obtain the test specimens.

Example 1	100.0	50.5	5.41	28.4	500.0	200.0	20.0	21.0	250.0	1
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Table 1 lists the principal components of the steel of this invention, and Table 2 shows other components and an A_{c1} and A_{c3} transformation temperature. These steels were austenitized at 980°C followed by cooling in air and tempering at 600°C for 1 hour. The resulting steels were analyzed to determine the presence of δ -ferrite phase, the mechanical properties, and the anti-stress corrosion cracking property. The results are summarized in Table 3. The temper parameter of the tempering in Example 1 was 17460. The δ -ferrite phase was not detected in any specimens except for the steel Nos. 5, 8, and 14 where a slight amount of δ -ferrite phase was observed. As for the Cu precipitation, observation by an electron microscope with a magnitude of 100,000 was conducted immediately after the tempering to confirm that fine Cu grains having the approximate size range of from 0.001 to 0.10 micron were uniformly dispersed on the whole matrix area. The degree of dispersion was counted as being approximately 30 to 100 fine Cu precipitate grains per 1 square micron of the matrix surface.

For all the steel specimens tested, the 0.2% yield stress and the Charpy impact energy at 0°C were above the target level, 75 kg/mm² and 10 kg-m, respectively. The anti-stress corrosion cracking property was tested and was found to conform to TMO 1-77 of the NACE (National Association of Corrosion Engineers) Standard. Following the procedure of the Standard, a specimen was immersed into a mixture of 5% NaCl solution and 0.5% acetic acid aqueous solution saturated with H_2S gas of 1 atm, and the specimen was subjected to a load of 60% to the 0.2% yield stress (for example, steel No. 1 in Table 3 was subjected to a load of $76 \times 0.6 = 45.6$ kg/mm²). The time to failure on SSC (Sulphide Stress Corrosion test) was determined. The results are summarized in Table 3 "SSC hours". As can be seen in Table 3, no steel among the steel Nos. 1 through 16 failed before 720 hours had passed.

In the evaluation of the corrosion resistance to CO_2 , a specimen was immersed into a 10% NaCl aqueous solution in an autoclave at 200°C , 30 atm, H_2S partial pressure of 0.05 atm, for 336 hours. Then, the mass loss was determined. For all the steels Nos. 1 to 16, the mass loss was 0.5 g/m² or less, which was considerably lower than 1.0 g/m², which was the minimum required level for conventional martensite stainless steels. Consequently, the steels of this invention were confirmed to have excellent corrosion resistance.

Table 1

Steel No.	Chemistry (principal elements, wt%)									
	C	Si	Mn	P	S	Ni	Cr	Mo	N	Cu
1	0.025	0.16	0.05	0.009	0.002	4.86	14.7	2.07	0.002	0.35
2	0.024	0.15	0.05	0.008	0.002	4.83	14.8	2.06	0.002	1.82
3	0.023	0.14	0.05	0.007	0.002	4.77	14.8	2.07	0.002	2.63
4	0.025	0.15	0.05	0.009	0.002	4.85	14.7	2.04	0.002	3.95
5	0.023	0.14	0.05	0.007	0.002	4.77	15.5	1.23	0.002	2.63
6	0.022	0.17	0.07	0.007	0.002	4.96	14.1	2.06	0.002	2.61
7	0.022	0.17	0.08	0.011	0.002	4.81	14.2	2.06	0.002	2.62
8	0.026	0.16	0.06	0.009	0.002	4.88	15.1	2.04	0.002	2.61
9	0.027	0.16	0.05	0.009	0.002	4.86	14.1	2.07	0.002	2.65
10	0.024	0.15	0.05	0.008	0.002	4.83	14.3	2.06	0.002	2.62
11	0.022	0.15	0.05	0.009	0.002	4.82	14.2	2.02	0.002	2.65
12	0.024	0.15	0.05	0.008	0.002	4.83	14.3	1.06	0.002	2.63
13	0.023	0.15	0.05	0.011	0.002	4.85	14.2	2.04	0.002	2.65
14	0.017	0.47	0.05	0.010	0.002	7.21	14.7	2.01	0.004	1.03
15	0.013	0.17	0.17	0.009	0.002	4.19	15.8	0.30	0.004	1.02
16	0.053	0.16	0.18	0.009	0.002	0.78	12.2	2.42	0.003	1.98

Table 2

Steel No.	Chemistry (principal elements, wt%)							Transformation temperature (°C)	
	Nb	V	Al	W	Ti	Ta	Ca	Ac3	Ac1
1	-	-	0.024	-	-	-	-	710	610
2	-	-	0.025	-	-	-	-	730	630
3	-	-	0.028	-	-	-	-	730	630
4	-	-	0.023	-	-	-	-	740	640
5	-	-	0.028	1.96	-	-	-	730	630
6	-	-	0.021	-	0.20	-	-	730	630
7	-	0.20	0.021	-	-	-	-	730	630
8	0.05	-	0.022	-	-	-	-	730	630
9	-	-	0.024	-	-	0.05	-	730	630
10	-	-	0.025	-	-	-	0.005	730	630
11	0.02	-	0.024	-	-	0.05	-	730	630
12	-	-	0.025	2.13	-	-	0.005	730	630
13	0.01	0.15	0.023	-	-	-	0.004	730	630
14	-	-	0.021	-	-	-	-	700	600
15	-	-	0.020	-	-	-	-	750	650
16	-	-	0.025	-	-	-	-	850	760

55 Example 2

10:

temperature). In all cases, the steel was austenitized followed by cooling in air, and tempering at 600 °C for 1 hour. The temper parameter at the tempering in Example 2 was 17460. When the austenitization temperature stayed with the range specified for this invention, the performance obtained was satisfactory. However, when the austenitization temperature was as low as 700 °C, the insufficient austenitization resulted in a poor performance with characteristics lower than the target level. When the austenitization temperature was as high as 1000 °C, the level of toughness obtained was low and the anti-stress corrosion cracking property was also poor.

Example	Austenitization temperature (°C)	Tempering temperature (°C)	Tempering time (h)	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Impact energy (J)	Anti-stress corrosion cracking (ASCC)
1	700	600	1	420	520	20	10	Low
2	800	600	1	450	550	20	15	Low
3	850	600	1	480	580	20	20	Low
4	900	600	1	500	600	20	25	Low
5	950	600	1	520	620	20	30	Low
6	1000	600	1	550	650	20	35	Low
7	1050	600	1	580	680	20	40	Low
8	1100	600	1	600	700	20	45	Low
9	1150	600	1	620	720	20	50	Low
10	1200	600	1	650	750	20	55	Low
11	1250	600	1	680	780	20	60	Low
12	1300	600	1	700	800	20	65	Low
13	1350	600	1	720	820	20	70	Low
14	1400	600	1	750	850	20	75	Low
15	1450	600	1	780	880	20	80	Low
16	1500	600	1	800	900	20	85	Low
17	1550	600	1	820	920	20	90	Low
18	1600	600	1	850	950	20	95	Low
19	1650	600	1	880	980	20	100	Low
20	1700	600	1	900	1000	20	105	Low
21	1750	600	1	920	1020	20	110	Low
22	1800	600	1	950	1050	20	115	Low
23	1850	600	1	980	1080	20	120	Low
24	1900	600	1	1000	1100	20	125	Low
25	1950	600	1	1020	1120	20	130	Low
26	2000	600	1	1050	1150	20	135	Low
27	2050	600	1	1080	1180	20	140	Low
28	2100	600	1	1100	1200	20	145	Low
29	2150	600	1	1120	1220	20	150	Low
30	2200	600	1	1150	1250	20	155	Low
31	2250	600	1	1180	1280	20	160	Low
32	2300	600	1	1200	1300	20	165	Low
33	2350	600	1	1220	1320	20	170	Low
34	2400	600	1	1250	1350	20	175	Low
35	2450	600	1	1280	1380	20	180	Low
36	2500	600	1	1300	1400	20	185	Low
37	2550	600	1	1320	1420	20	190	Low
38	2600	600	1	1350	1450	20	195	Low
39	2650	600	1	1380	1480	20	200	Low
40	2700	600	1	1400	1500	20	205	Low
41	2750	600	1	1420	1520	20	210	Low
42	2800	600	1	1450	1550	20	215	Low
43	2850	600	1	1480	1580	20	220	Low
44	2900	600	1	1500	1600	20	225	Low
45	2950	600	1	1520	1620	20	230	Low
46	3000	600	1	1550	1650	20	235	Low
47	3050	600	1	1580	1680	20	240	Low
48	3100	600	1	1600	1700	20	245	Low
49	3150	600	1	1620	1720	20	250	Low
50	3200	600	1	1650	1750	20	255	Low

Example 2

The test condition was the same as in Example 1. The test result is shown in Table 2. As in this case, steel No. 2 was used and the steel was austenitized followed by cooling in air, and tempered at 600 °C for 1 hour.

Table 4

Test Name	Quench hardening temperature (°C)	Tempering temperature (°C)	Tempering time (hour)	T.P.	Size of Cu precipitate (micron)	0.2% yield stress (kg/mm ²)	CVN (kg-m)	SSC (hour)	Total Judgment
Example 2 (Steel No. 3)	700	600	1.00	17460	0.001-0.1 micron	73	13	> 720	X
	850					82	12	> 720	O
	900					83	13	> 720	O
	980					82	14	> 720	O
	1000					86	7	< 100	X
Example 3 (Steel No. 3)	950	450	1.00	14460	No precipitation occurred	101	7	< 100	X
		500		15460	0.001-0.1 micron	107	10	> 720	O
		550		16460		104	10	> 720	O
		600		17460		83	13	> 720	O
		630		18060		70	14	> 720	O
		350		18460	No precipitation occurred	64	13	> 720	X

- (Note 1) In all cases, no δ -ferrite phase appeared.
(Note 2) CVN designates the Charpy impact energy at 0°C.
(Note 3) SSC designates the fracture time.
(Note 4) T.P. designates the temper parameter.
(Note 5) Symbol mark of "O" means "satisfactory".
Symbol mark of "X" means "poor".

Example 3

The test condition was the varied tempering temperature while maintaining the austenitization temperature at 950 °C. The result is shown in a part of Table 4. Also in this case, steel No. 3 was used, and the steel was austenitized followed by cooling in air, and tempering at 600 °C for 1 hour.

When the tempering temperature stayed within a range of this invention, the performance obtained was favorable. However, when the tempering temperature was 450 °C, lower than the range of this invention, the martensite structure stayed in a hard and brittle state, so the toughness was poor and the anti-stress corrosion cracking property was also poor.

Furthermore, no Cu precipitation occurred. On the other hand, when the tempering temperature was 650 °C, higher than the Ac₁ point, fine Cu precipitate grains were not present because they had dissolved again, so the strength was decreased.

Example 4

In Example 4, the effect of the temper parameter as a variable of tempering was observed. Also in this case, steel No. 5 was austenitized followed by cooling in air, and tempering at a temperature range of from 450 to 680 °C. The results are shown in Table 5.

As seen in Table 5, even when the tempering temperature was 500 °C, the Charpy impact energy was lower than the target level if the tempering time was as short as 0.10 hour (giving the temper parameter of 14690). On the other hand, when the tempering time was 0.5 hours or longer, the temper parameter became 15200 or more, which gave sufficient strength and toughness and a favorable anti-stress corrosion cracking property.

In the case that the tempering temperature was 550 °C, the tempering was carried out within a temper parameter range of from 15200 to 17800, and the target level was attained.

When the tempering temperature was 600 °C, a steel processed under a tempering time of 1.0 hour gave a temper parameter range of from 15200 to 17800, so the target level of performance was attained. However, a steel treated at the tempering time of 5 hrs gave a temper parameter of above 17800, which suggests that the Cu precipitate had dissolved again or had coarse grains to resulting in a degradation of the strength and to an insufficient anti-stress corrosion cracking property.

Tempering Temperature (°C)	Tempering Time (hr)	Temper Parameter	Tensile Strength (MPa)	Yield Strength (MPa)	Charpy Impact Energy (J)	Anti-stress Corrosion Cracking Property
450	0.10	14690	1010	700	10	Not Satisfactory
450	0.20	14690	1010	700	10	Not Satisfactory
450	0.50	15200	1010	700	10	Not Satisfactory
450	1.00	15200	1010	700	10	Not Satisfactory
450	5.00	17800	1010	700	10	Not Satisfactory
500	0.10	15200	1010	700	10	Not Satisfactory
500	0.20	15200	1010	700	10	Not Satisfactory
500	0.50	15200	1010	700	10	Not Satisfactory
500	1.00	15200	1010	700	10	Not Satisfactory
500	5.00	17800	1010	700	10	Not Satisfactory
550	0.10	15200	1010	700	10	Not Satisfactory
550	0.20	15200	1010	700	10	Not Satisfactory
550	0.50	15200	1010	700	10	Not Satisfactory
550	1.00	15200	1010	700	10	Not Satisfactory
550	5.00	17800	1010	700	10	Not Satisfactory
600	0.10	15200	1010	700	10	Not Satisfactory
600	0.20	15200	1010	700	10	Not Satisfactory
600	0.50	15200	1010	700	10	Not Satisfactory
600	1.00	15200	1010	700	10	Not Satisfactory
600	5.00	17800	1010	700	10	Not Satisfactory

Comparative Example 1: A steel processed under a tempering time of 0.10 hour at 500 °C, which gave a temper parameter of 14690, was used as a comparative example. The results are shown in Table 6. The Charpy impact energy was lower than the target level, and the anti-stress corrosion cracking property was also poor.

Table 5

Quench hardening temperature (°C)	Tempering temperature (°C)	Tempering time (hour)	T.P.	Size of Cu precipitate (micron)	0.2% yield stress (kg/mm ²)	CVN (kg-m)	SSC (hour)	Total judgment
950	450	0.25	14020	No precipitation occurred	102	3	<100	X
		0.10	14590	0.001-0.1 micron	104	7	<100	X
			15230		106	11	>720	O
	500	5.00	16000		108	10	>720	O
		1.00	16460		103	12	>720	O
	550	5.00	17040		92	13	>720	O
		1.00	17460		83	12	>720	O
	600	5.00	18070	coarse	70	13	<100	X
		1.00	18460	No precipitation occurred	63	12	<100	X
	650	5.00	19110		57	13	<100	X
		5.00	19730		55	10	<100	X
	680	5.00						

- (Note 1) In all cases, no δ -ferrite phase appeared.
 (Note 2) CVN designates the Charpy impact energy at 0°C.
 (Note 3) SSC designates the fracture time.
 (Note 4) T.P. designates the temper parameter.
 (Note 5) Symbol mark of "O" means "satisfactory"
 Symbol mark of "X" means "poor".

Comparative Example

Among the Comparative Examples, those which used steels having a composition which is outside the specified range of this invention are listed in Tables 6 and 7 in terms of their composition and test results. The applied austenitization temperature and tempering treatment are the same as in Example 1. Since the

steels in Table 6 had at least one component present in an amount outside of the specified range of this invention, the test results gave lower levels of strength or toughness than the target levels of this invention. As a result, the target level of this invention for the anti-stress corrosion cracking property could not be attained. Steels (a) and (b) contained Cu at below 0.3%, and no Cu precipitate was formed, which resulted in a strength of less than 75 kg/mm². Steel (c) contained Cu at above 4.0%, and it suffered cracks during the hot-rolling stage which leads to a significant degradation of the commercial value of the product. Steel (c) also showed a poor SSC characteristic. Steel (d) had a low Ni content, and steel (g) had high content of Cr and Mo, and steel (i) had a high content of Mo, so they gave delta-ferrite phase over 10% of area ratio, which significantly degraded the toughness. Steel (e) had Ni content above 9%, so that the steel was very expensive.

Therefore, steel (e) was inadequate for the object of this invention. Also steel (e) was inferior in SSC performance. Steel (f) had a low Cr content and steel (h) had a low Mo content, so those steels were inferior in corrosion-resistance to CO₂. Steel (j) had a high C content so that the SSC performance was poor.

	C	Si	Mn	P	S	Al	Ni	Cr	Mo	Cu	Co	Other	Remarks
15	0.05	0.03	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
20	0.05	0.03	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
25	0.05	0.03	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
30	0.05	0.03	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
35	0.05	0.03	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
40	0.05	0.03	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
45	0.05	0.03	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
50	0.05	0.03	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	

Table 6

Steel No.	Chemistry (wt%)									
	C	Si	Mn	P	S	Ni	Cr	Mo	N	Cu
a	0.024	0.15	0.05	0.008	0.002	4.81	14.8	2.06	0.002	0.02
b	0.026	0.16	0.06	0.009	0.002	4.88	14.7	2.04	0.002	0.023
c	0.023	0.15	0.05	0.007	0.002	4.96	14.8	2.06	0.002	0.026
d	0.024	0.14	0.09	0.007	0.002	0.37	14.8	2.07	0.002	0.027
e	0.025	0.13	0.09	0.007	0.002	9.97	14.8	2.06	0.002	0.026
f	0.024	0.14	0.09	0.008	0.002	4.81	10.8	2.06	0.002	0.021
g	0.026	0.16	0.06	0.011	0.002	1.88	18.7	3.04	0.002	0.023
h	0.025	0.16	0.05	0.012	0.002	4.86	14.7	0.05	0.002	0.024
i	0.024	0.17	0.09	0.008	0.002	4.83	15.8	3.53	0.002	0.025
j	0.085	0.17	0.05	0.009	0.002	4.85	14.7	2.04	0.002	0.023

The material analysis sheet of any one of listing 7 to 10 within the MC control is from 0.30 to 0.50

SAS WAC

55 1. A high strength martensitic stainless steel consisting essentially of: 32

- impurities,

said steel having an area ratio of δ -ferrite phase of at most 10 %; and
 said steel having fine copper precipitates dispersed in a matrix.

2. The martensitic stainless steel of claim 1, wherein the C content is from 0.013 to 0.053 wt.%. 5
3. The martensitic stainless steel of claims 1 or 2, wherein the Cr content is from 12.2 to 15.8 wt.%. 10
4. The martensitic stainless steel of any one of claims 1 to 3 wherein the Si content is from 0.14 to 0.47 wt.%. 15
5. The martensitic stainless steel of any one of the preceding claims wherein the Mn content is from 0.05 to 1.05 wt.%. 20
6. The martensitic stainless steel of any one of the preceding claims wherein the Ni content is from 0.78 to 7.21 wt.%. 25
7. The martensitic stainless steel of any one of the preceding claims wherein the Mo content is from 0.30 to 2.42 wt.%. 30
8. The martensitic stainless steel of any one of the preceding claims wherein said steel has an area ratio of δ -ferrite phase of at most 3 %. 35
9. The martensitic stainless steel of any one of the preceding claims wherein said steel includes at least 30 of copper precipitates having 0.1 micron or less in diameter per 1 square micron. 40
10. The martensitic stainless steel of any one of the preceding claims wherein said steel has 0.2 % yield stress of 75 kg/mm² or more and charpy impact energy of 10 kg-m or more. 45
11. A high strength martensitic stainless steel consisting essentially of:
 0.06 wt.% or less C, 12 to 16 wt.% Cr, 1 wt.% or less Si, 2 wt.% or less Mn, 0.5 to 8 wt.% Ni, 0.1 to 2.5 wt.% Mo, 0.3 to 4 wt.% Cu, 0.05 wt.% or less N, at least one element selected from the group consisting of 0.01 to 0.1 wt.% V and 0.01 to 0.1 wt.% Nb and the balance being Fe and inevitable impurities;
 said steel having an area ratio of δ -ferrite phase of 10 % or less; and
 said steel having fine copper precipitates dispersed in a matrix. 50
12. The martensitic stainless steel of claim 11, wherein the C content is from 0.013 to 0.053 wt.%. 55
13. The martensitic stainless steel of claims 11 or 12 wherein the Cr content is from 12.2 to 15.8 wt.%. 60
14. The martensitic stainless steel of any one of claims 11 to 14 wherein the Si content is from 0.14 to 0.47 wt.%. 65
15. The martensitic stainless steel of any one of claims 11 to 14 wherein the Mn content is from 0.05 to 1.05 wt.%. 70
16. The martensitic stainless steel of any one of claims 11 to 15 wherein the Ni content is from 0.78 to 7.21 wt.%. 75
17. The martensitic stainless steel of any one of claims 11 to 16 wherein the Mo content is from 0.30 to 2.42 wt.%. 80
18. The martensitic stainless steel of any one of claims 11 to 17 wherein said steel has an area ratio of δ -ferrite phase of at most 3 %. 85
19. The martensitic stainless steel of any one of claims 11 to 18 wherein said steel includes at least 30 of copper precipitates having 0.1 micron or less in diameter per 1 square micron. 90

20. The martensitic stainless steel of any one of claims 11 to 19 wherein said steel has 0.2 % yield stress of 75 kg/mm² or more and Charpy impact energy of 10 kg-m or more.
21. A method for manufacturing a high strength martensitic stainless steel comprising the steps of:
 5 preparing a martensitic stainless steel consisting essentially of 0.06 wt.% or less C, 12 to 16 wt.% Cr, 1 wt.% or less Si, 2 wt.% or less Mn, 0.5 to 8 wt.% Ni, 0.1 to 2.5 wt.% Mo, 0.3 to 4 wt.% Cu, 0.05 wt.% or less N, and the balance being Fe and inevitable impurities;
 austenitizing said martensitic stainless steel at a temperature of A_{c3} transformation point to 980 °C to produce an austenitized martensitic steel;
 10 cooling the austenitized martensitic stainless steel;
 tempering the cooled stainless steel to disperse fine Cu precipitate grains in a matrix at a tempering temperature (T °C) of between 500 °C to the lower one of either 630 °C or A_{c1} transformation point and at a tempering time (t hour), said tempering temperature and said tempering time satisfying the following equation;
 15 $15200 \leq (20 + \log t)(273 + T) \leq 17800$;
22. The method of claim 21, wherein said A_{c3} transformation point is from 700 to 850 °C.
23. The method of claim 21, wherein said A_{c1} transformation point is from 600 to 760 °C.
24. The method of any one of claims 21 to 23, wherein said tempering temperature (T °C) and said tempering time (t hour) satisfying the following equation;
 25 $15500 \leq (20 + \log t)(273 + T) \leq 17000$;
25. The method of any one of claims 21 to 24 wherein the C content of the stainless steel is from 0.013 to 0.053 wt.%;
- 30 26. The method of any one of claims 21 to 25 wherein the Cr content of the stainless steel is from 12.2 to 15.8 wt.%;
27. The method of any one of claims 21 to 26 wherein the Si content of the stainless steel is from 0.14 to 0.47 wt.%;
- 35 28. The method of any one of claims 21 to 27, wherein the Mn content of the stainless steel is from 0.05 to 1.05 wt.%;
29. The method of any one of claims 21 to 28 wherein the Ni content of the stainless steel is from 0.78 to 7.21 wt.%;
- 40 30. The method of any one of claims 21 to 29 wherein the Mo content of the stainless steel is from 0.30 to 2.42 wt.%;
- 45 31. A method for manufacturing a high strength martensitic stainless steel comprising the steps of:
 preparing a martensitic stainless steel consisting essentially of 0.06 wt.% or less C, 12 to 16 wt.% Cr, 1 wt.% or less Si, 2 wt.% or less Mn, 0.5 to 8 wt.% Ni, 0.1 to 2.5 wt.% Mo, 0.3 to 4 wt.% Cu, 0.05 wt.% or less N, at least one element selected from the group consisting of 0.01 to 0.1 wt.% V and 0.01 to 0.1 wt.% Nb and the balance being Fe and inevitable impurities;
 50 austenitizing said martensitic stainless steel at a temperature of A_{c3} transformation point to 980 °C to produce an austenitized martensitic steel;
 cooling the austenitized martensitic stainless steel;
 tempering the cooled stainless steel to disperse fine Cu precipitate grains in a matrix at a tempering temperature (T °C) of between 500 °C to the lower one of either 630 °C or A_{c1} transformation point and at a tempering time (t hour), said tempering temperature and said tempering time
 55 satisfying the following equation;
 $15200 \leq (20 + \log t)(273 + T) \leq 17800$.

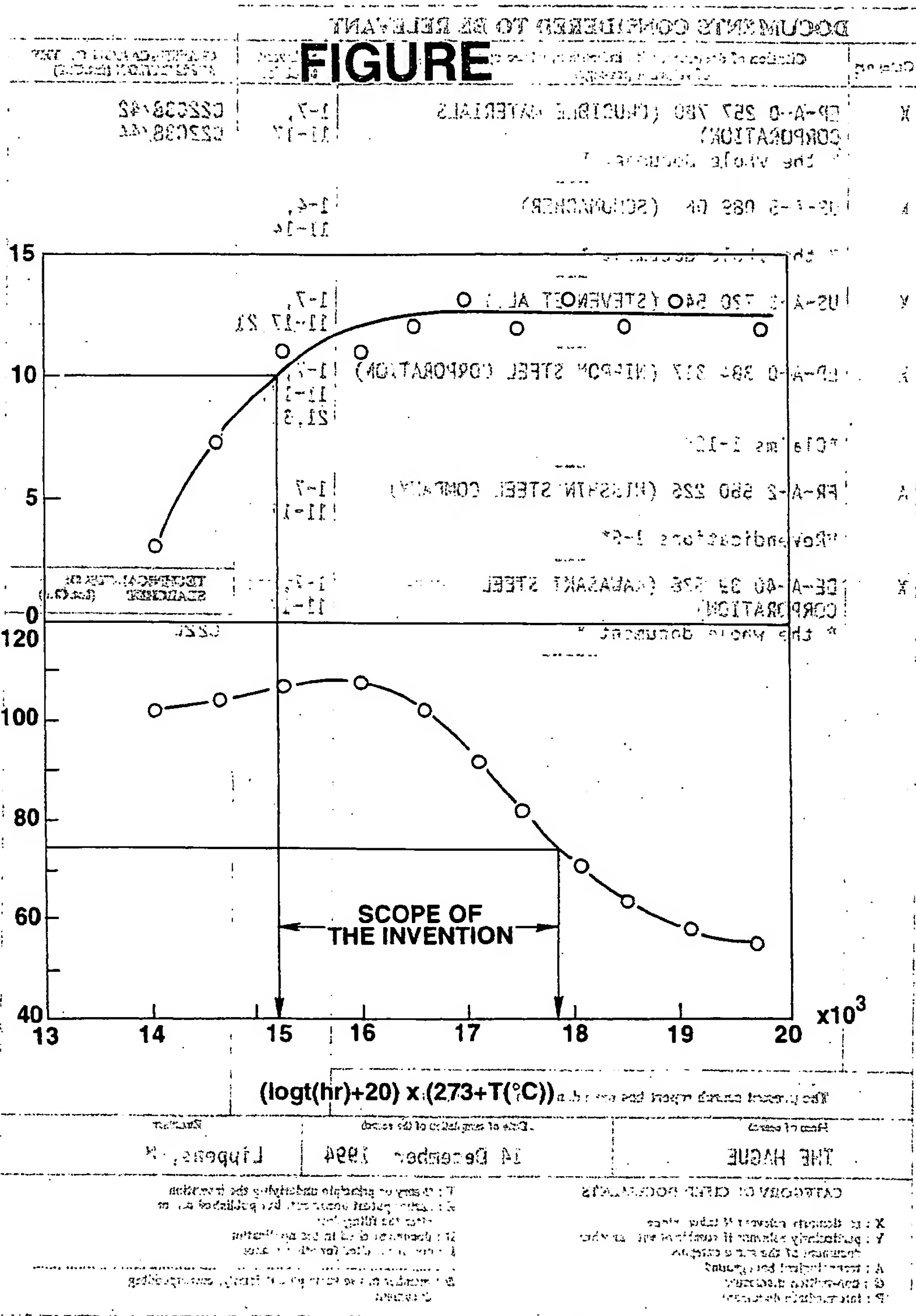
32. The method of claim 31, wherein said A_{c3} transformation point is from 700 to 850 °C.
33. The method of claim 31, wherein said A_{c1} transformation point is from 600 to 760 °C.
34. The method of any one of claims 31 to 33 wherein said tempering temperature (T_p °C) and said tempering time (t hour) satisfying the following equation:

$$15500 \leq (20 + \log t)(273 + T_p) \leq 17000$$
35. The method of any one of claims 31 to 34, wherein the C content of the stainless steel is from 0.013 to 0.053 wt. %.
36. The method of any one of claims 31 to 35, wherein the Cr content of the stainless steel is from 12.2 to 15.8 wt. %.
37. The method of any one of claims 31 to 36 wherein the Si content of the stainless steel is from 0.14 to 0.47 wt. %.
38. The method of any one of claims 31 to 37 wherein the Mn content of the stainless steel is from 0.05 to 1.05 wt. %.
39. The method of any one of claims 31 to 38 wherein the Ni content of the stainless steel is from 0.78 to 7.21 wt. %.
40. The method of any one of claims 31 to 39 wherein the Mo content of the stainless steel is from 0.30 to 2.42 wt. %.
41. The use of high strength martensitic stainless steel according to any one of claims 1 to 20 in an environment containing CO₂ and/or H₂S.
42. The use according to claim 41 in drilling or transporting crude oil or natural gas.

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EUROPEAN SEARCH REPORT

Application Number
EP 94 11 6644

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 257 780 (CRUCIBLE MATERIALS CORPORATION) * the whole document *	1-7, 11-17	C22C38/42 C22C38/44
X	US-A-5 089 067 (SCHUMACHER) * the whole document *	1-4, 11-14	
X	US-A-3 720 545 (STEVENET AL.)	1-7, 11-17, 21	
X	EP-A-0 384 317 (NIPPON STEEL CORPORATION) *Claims 1-12*	1-7, 11-17, 21, 31	
A	FR-A-2 550 226 (NISSHIN STEEL COMPANY) *Revendications 1-6*	1-7, 11-17	
X	DE-A-40 39 538 (KAWASAKI STEEL CORPORATION) * the whole document *	1-7, 11-17	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C22C
The present search report has been drawn up for all claims X (OS+T) (YGO)			
Place of search THE HAGUE		Date of completion of the search 14 December 1994	Examiner Lippens, M
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